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DIRECTORATE OF CHEMICAL DEFENCE RESEARCH AND DEVELOPMENT

CHEMICAL DEFENCE EXPERIMENTAL ESTABLISHMENT

THE KINETICS OF THE THERMAL DECOMPOSITION OF ISOPROPYL METHYLPHOSPHONOFUORIDATE

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P.T.P. 442

The Kinetics of the Thermal Decomposition of Isopropyl
Methylphosphonofluoridate

Part II

Further Studies on the reactions involved and their mechanisms

by

D.J. Marsh

Corrigenda

Page 10, last para. Amend to read:

"The values of the rate constants in Table V are in reasonable agreement with the value obtained in Table III, viz. 2.99×10^{-2} hours⁻¹".

Page 13, para. 3. Insert at end of paragraph:

"However, at ordinary temperatures the rate of attainment of equilibrium will be too low to affect storage life seriously. It is estimated that at 25°C, the times for 1% and 10% decomposition by disproportionation are about 14 months and 12 years respectively. These figures are derived for pure GB in the absence of base. With stabilised technical GB, the times may be very much greater."

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Porton Technical Paper No. 442

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Date 13 OCT 1954

The Kinetics of the Thermal Decomposition of Isopropyl
Methylphosphonofluoridate.

Part II

Further Studies on the reactions involved and their mechanisms

by

D.J. Marsh

SUMMARY

1. Further work on the thermal decomposition of isopropyl methylphosphonofluoridate (GB) has shown that the reactions involved differ in some respects from the scheme previously suggested.
2. The data previously obtained have been reconsidered in accordance with the later findings and new values for the rate constants obtained. Values of the equilibrium constant for the disproportionation reaction have also been calculated.
3. Experiments carried out have not enabled the mechanism of the disproportionation reaction to be elucidated and the significance of the rate constants obtained for this reaction is by no means clear.
4. The results obtained for the propene evolution reaction do not differ significantly from those previously obtained and the main conclusions of earlier reports still hold good.

(Sgd.) T.C. Nugent,
Acting Head, Chemistry Section.

(Sgd.) E.A. Perren,
Supt., Research Division.

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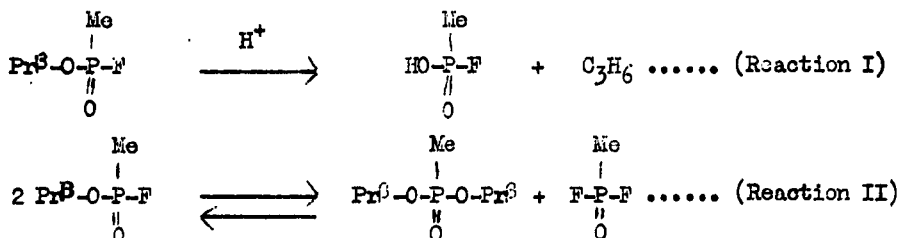
1. Introduction

The kinetics of the thermal decomposition of GB have been previously studied and reported (Part I; Porton Technical Paper No. 265). The mechanisms of the reactions involved have also been discussed by Bevan and Hudson (Porton Technical Paper No. 330). Chemical aspects of the storage stability of GB have also been investigated (Porton Technical Paper No. 381).

Experiments carried out subsequently have shown, however, that the reactions occurring in the decomposition differ in some respects from those given in the previous report (P.T.P. 265).

An account of these experiments and of other investigations into the mechanisms of the reactions involved is given in this report.

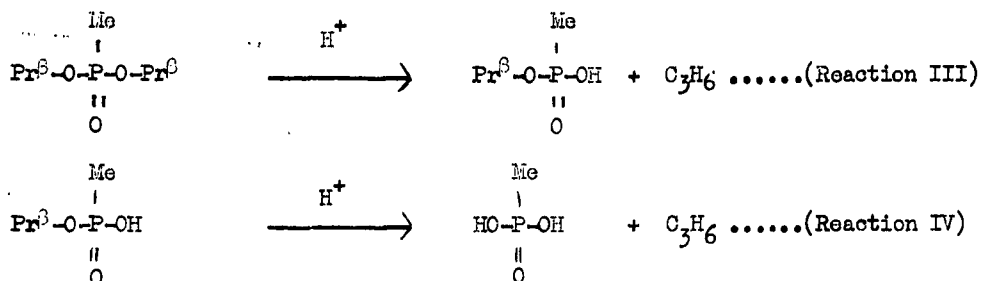
The two main reactions now considered to occur during the thermal decomposition of GB are:-



Of these reactions, the first is acid catalysed and hence autocatalytic and does not occur spontaneously. The second is reversible and is also acid catalysed in both directions.

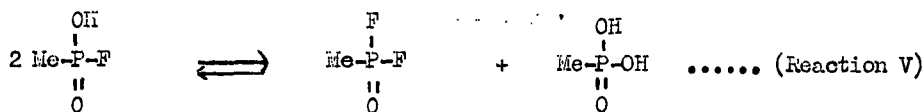
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The di-isopropyl methylphosphonate formed in reaction II was previously thought to undergo further decomposition in two stages:-



It will be shown, however, that the decomposition of the di-ester is not catalysed by the acids which may be present in the system, and hence these two reactions need not be considered further from the point of view of the decomposition of GB.

A further possible reaction, the disproportionation of methylphosphonofluoric acid, was shown to be reversible:-



For reasons previously discussed (P.T.P. 265), this reaction will not play an appreciable part in the decomposition of GB.

2. Experimental Procedure

The apparatus, and methods for following the decomposition, used have been described previously (P.T.P.'s 265 and 381).

The GB used was laboratory prepared material which had been purified by redistillation until the apparent acidity was less than one part per million of hydrogen ion.

Isopropyl hydrogen methylphosphonate, methylphosphonofluoric acid, methylphosphonic difluoride and di-isopropyl methylphosphonate were redistilled immediately before use.

3. The Kinetics of the reactions involved in the decomposition of GB.

- (a) Reaction I. The previous conclusions (P.T.P. 265) that this is a bimolecular catalysed reaction, and hence auto catalytic, still hold good. No spontaneous decomposition of GB by this reaction is thought to occur.
- (b) Reaction II. It was previously thought that this reaction proceeded in the forward direction only, the product di-isopropyl methylphosphonate being removed by reactions III and IV. It will be shown later in the report however, that these reactions do not occur in the system, and hence the reverse reaction II must be considered.

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Both the forward and reverse reactions involve two molecules. The mechanisms suggested for the reaction involve an initial ionisation stage for the forward reaction (see discussion section). This would be comparatively slow and in the early stages of the decomposition would be rate determining and so giving first order kinetics. Subsequently, however, when the amount of GB present has fallen the ionisation stage may no longer be rate determining and second order kinetics would be observed.

Addition of di-isopropyl methylphosphonate to technical GB did not reduce the amount of decomposition by mass action effect on reaction II (see Appendix VI to P.T.P. 381). It may be that the di-ester is not involved in the rate-determining stage in the reverse reaction. The separation of a fluoride ion from methylphosphonic difluoride could be the rate determining stage, being analogous to that suggested for the forward reaction. If this is so, the reverse reaction would show first order kinetics under suitable conditions where a sufficient excess of di-ester is present. In the actual decomposition of GB this is probably not the case and 2nd. order kinetics are probably obeyed, especially in the early stages where the concentrations of difluoride and di-ester are small.

Experimental verification of the kinetics of reaction II would be extremely difficult as it has not been found possible to isolate this reaction from the auto catalytic reaction I which plays a much greater part in the decomposition. At more moderate temperatures ca. 60°C. the disproportionation reaction is more important, but the reactions are very slow and it is doubtful whether the attempt would be worth while.

Equations for the disappearance of GB and the appearance of propene and di-ester may be written as follows:-

$$-\frac{d[GB]}{dt} = k_c [GB] [MePO(F)(OH)] + k_d [GB] - k'_d [MePOF_2] [MePO(OPr)_2]$$

$$\frac{d[C_3H_6]}{dt} = k_c [GB] [MePO(F)(OH)]$$

$$\frac{d[MePOF_2]}{dt} = \frac{d[MePO(OPr)_2]}{dt} = k_d [GB] - k'_d [MePOF_2] [MePO(OPr)_2]$$

If we put $G = [GB]$, $M = [MePO(F)(OH)] = [C_3H_6]$ and

$F = [MePOF_2] = [MePO(OPr)_2]$ we may write :-

$$-\frac{dG}{dt} = k_c GM + k_d G - k'_d F^2 \quad \dots \dots \dots (1)$$

$$\frac{dM}{dt} = k_c GM \quad \dots \dots \dots (2)$$

$$\frac{dF}{dt} = k_d G - k'_d F^2 \quad \dots \dots \dots (3)$$

No satisfactory solution of these equations is possible.

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The above equations are applicable in the early stages of the decomposition. When the decomposition has proceeded so that about half of the original GB has decomposed, it is unlikely, as has already been discussed, that the forward disproportionation reaction still shows first order kinetics. In this case equations (1) and (3) must be replaced by:-

$$-\frac{dG}{dt} = k_c GM + k_d \left(\frac{G}{2}\right)^2 - k'_d F^2 \quad \dots\dots\dots (1a)$$

and

$$\frac{dF}{dt} = k_d \left(\frac{G}{2}\right)^2 - k'_d F^2 \quad \dots\dots\dots (3a)$$

In these equations no account is taken of the catalysis of reaction II by acid. If, as is discussed later, the effect of acid is to facilitate the separation of a fluoride ion from GB or the difluoride, then as the catalysis is small compared with that on reaction I it can probably be neglected in the early stages, whereas in the later stages the separation of the fluoride ion is probably not rate determining.

It is found that the concentration of di-ester and difluoride reaches a maximum as the decomposition proceeds. (See figures 1-3), and then falls off fairly rapidly. At this maximum the net rate of formation of di-ester and difluoride is zero and hence:-

$$\frac{dF}{dt} = 0$$

$$\text{and} \quad k_d \left(\frac{G}{2}\right)^2 = k'_d F^2$$

$$\therefore \quad \frac{k_d}{k'_d} = \frac{F^2}{\left(\frac{G}{2}\right)^2} = K_d$$

where K_d is the equilibrium constant for reaction II.

It is clear that no true equilibrium will be set up in this reaction, but as at lower temperatures the rate of reaction I is negligible the value of K_d will be of some practical importance.

4. Validity of the results given previously and determination of new rate constants.

Since it is now known that the reverse reaction II must be considered in the decomposition of GB, it is clear that the validity of the values of the rate constants calculated by the procedure given in P.T.P. 265 is questionable. Failure to take this reaction into account presumably leads to low values for the rate constants for the forward reaction II. The effect on the values of the rate constants for reaction I is not readily seen, although it may be small.

No method of calculating rate constants using the above equations can be found, but estimates may be made from the slopes of the graphs showing plots of G and M against time, since the values of G and M at a given time are known and also the values of F can be obtained by difference. The accuracy of the figures obtained will be low.

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Initially, with pure GB, $F = 0$ and M is very small so that equation (1) simplifies to:-

$$-\frac{dG}{dt} = k_d G.$$

which enables a value for k_d to be obtained.

k_d can be obtained by measuring the slope of the gas evolution curves at various points and substituting the values in equation (2).

Finally, as already noted at the maximum point in the plot of F against time, we have $\frac{dF}{dt} = 0$ and hence:-

$$k_d = \frac{k_d}{k'_d} = \frac{P^2}{\left(\frac{G}{2}\right)^2}$$

The values obtained for k_d are given in Table I.

Table I
Evaluation of k_d .

80°C.			90°C.		
t(hrs.)	M	$k_d \times 10^3 (\text{hrs}^{-1})$	t(hrs.)	M	$k_d \times 10^2 (\text{hrs}^{-1})$
200	0.021	5.20	50	0.010	2.61
300	0.032	3.48	100	0.025	1.48
400	0.042	2.98	150	0.045	1.00
500	0.053	2.77	200	0.068	1.07
600	0.068	3.53	250	0.105	1.27
700	0.093	3.60	300	0.173	1.57
800	0.124	3.95	350	0.310	2.49
900	0.173	4.82	400	0.658	6.31
1000	0.253	6.78			
1100	0.407	11.2			
1200	0.682	19.3			
100°C.			120°C.		
t(hrs.)	M	$k_d \times 10^2 (\text{hrs}^{-1})$	t(hrs.)	M	$k_d (\text{hrs}^{-1})$
30	0.004	5.43	6	0.008	0.385
50	0.008	3.63	8	0.013	0.240
70	0.015	3.58	10	0.018	0.236
90	0.028	2.49	12	0.028	0.180
110	0.040	2.48	14	0.038	0.174
130	0.060	2.52	16	0.050	0.180
150	0.090	2.71	18	0.068	0.196
170	0.145	3.51	20	0.095	0.202
190	0.253	5.38	22	0.133	0.216
210	0.530	11.4	24	0.186	0.268
			26	0.298	0.448
			28	0.525	0.968

The values of M are expressed in moles/initial mole GB and so the units in which the rate constants are expressed are again hours^{-1} . This point as previously discussed (P.T.P. 265).

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It will be noted that the initial values for k_0 are somewhat high and that subsequently the values appear to increase as the reaction proceeds. Initially the accuracy of the gas evolution data is not great so that the high values are probably spurious. The subsequent increase in the rate constants is not surprising, as it must be remembered that as the reaction proceeds the medium in which it takes place is also changing, being initially pure GB and subsequently containing increasing amounts of the various decomposition products.

In view of these considerations, the initial high values and those later ones obtained for values of M greater than 0.2 have been ignored and the mean of the remainder taken. The values so obtained together with the previously accepted values (P.T.P. 265) are given in table III.

The values of k_d obtained from the initial slopes of the plots of G versus t (P.T.P. 265; Figures 5-8) are also given in table III. Since the values of G show appreciable scatter the accuracy of these figures is low.

Values of K_d , the equilibrium constant for the disproportionation reaction II, are obtained as described above from the data for the concentrations of reactants present when the concentration of difluoride is at a maximum. The derivation of these values is given in table II.

Table II

Evaluation of K_d .

Temperature °C.	Time at which maximum occurs hours	[GB] remaining = G moles/initial mole GB.	$[MePOF_2] = [MePO(OPr)_2]$ = F . moles/initial mole GB.	$K_d = \frac{F^2}{G}$	% GB in mixture in equilibrium
80	1100	0.453	0.070	0.096	76.4
90	340	0.567	0.0805	0.079	77.8
100	180	0.652	0.081	0.062	80.1

No maximum was reached in the times for which the experiments at 120° were conducted.

Values of the rate constants for the reverse reaction II k'_d , can be obtained from those for k_d and K_d . These are also given in Table III. Values so obtained are for the uncatalysed reverse reaction.

Table III

Values of the rate constants for the reactions occurring in the thermal decomposition of GB.

Temperature °C.	k_0 hrs ⁻¹		k_d hrs ⁻¹		K_d	k'_d hrs ⁻¹
	New Value	Previous Value (P.T.P. 265)	New Value	Previous Value (P.T.P. 265)		
80	3.59×10^{-3}	3.70×10^{-3}	1.1×10^{-4}	1.93×10^{-4}	0.096	1.1×10^{-3}
90	1.28×10^{-2}	1.18×10^{-2}	6.0×10^{-4}	5.66×10^{-4}	0.079	7.6×10^{-3}
100	2.99×10^{-2}	2.36×10^{-2}	3.3×10^{-4}	1.68×10^{-3}	0.062	5.3×10^{-3}
120	0.210	0.239	2.4×10^{-3}	7.65×10^{-3}	-	-

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Plots of the logarithms of the rate constants against the reciprocal of the absolute temperature are shown in figures 4 and 5. The variations of the constants with temperature may be expressed by the following equations, in which T is the absolute temperature:-

$$\log_{10} k_c = 14.6888 - \frac{6038.44}{T}$$

$$\log_{10} k_d = 7.7710 - \frac{4102.93}{T}$$

$$\log_{10} k'_d = 10.1088 - \frac{4556.97}{T}$$

$$\log_{10} K_d = \frac{1248.42}{T} - 4.5502$$

These equations were calculated by the method of least squares

The corresponding energies of activation are:-

	<u>New Value</u>	<u>Previous Value</u> (P.T.P. 265)
For reaction I	27.6 K.cals./mole	28.3 K.cals./mole
For forward reaction II	18.8 K.cals./mole	25.4 K.cals./moles
For reverse reaction II	20.8 K.cals./mole	-

The heat of reaction for the disproportionation determined from the values of K_d is 5.7 K.cals./mole.

As previously noted, the data from which the values of k_d are derived show appreciable scatter and as the plot of $\log k_d$ against $1/T$ also shows some scatter, the value for the activation energy for the forward disproportionation reaction can only be regarded as a rough approximation. It would, however, seem that the activation energy is rather lower than had been previously supposed.

Since the values of k'_d are derived from those of k_d and K_d , the accuracy of the value of the activation energy for the reverse reaction is even less.

The values of the activation energy for reaction I, and the heat of reaction II are regarded as reasonably accurate since the plots of $\log k_c$ and $\log K_d$ against $1/T$ show good linearity.

A value for K_d at 25°C. may be derived also from thermochemical data (E. Neale; P.T.P. 339).

The calculations involved are given in Appendix I. The value obtained for K_d at 25°C. is 1.003, and at this temperature the reaction mixture would contain 50% GB, 25% of methylphosphonic difluoride and 25% of di-isopropyl methylphosphonate.

The value of K_d at 25°C. obtained from the equation derived from the values from the kinetic data is 0.44. This would mean that the reaction mixture would contain 60% GB and 20% each of difluoride and di-ester. The agreement is fair considering the methods by which the values are obtained, and the assumptions involved.

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It may also be noted that the heat of the reaction from kinetic data in the temperature range 80-100°C. is 5.7 K.cal./mole, while that from the thermochemical data at 25°C. is 2 K.cal./mole. In view of the assumptions involved and the difference in temperatures at which the values are obtained the agreement between the two values is good.

5. Experiments on the reaction of methylphosphonic difluoride and di-isopropyl methylphosphonate (Reverse reaction II).

Preliminary experiments had shown that some GB was formed when a mixture of methylphosphonic difluoride and di-isopropyl methylphosphonate was heated together. It was soon found, however, that the GB formed subsequently decomposed by Reaction I. The difluoride is very hygroscopic and readily hydrolysed to acid, so the mixtures were made up in a dry box. Also with a view to retarding the decomposition of the GB formed, some experiments were carried out in the presence of a base or steel.

The results obtained, starting with an equimolar mixture of the di-ester and difluoride are given in Table IV.

Table IV

Reaction of methylphosphonic difluoride and di-isopropyl methylphosphonate

The two substances were present in equimolar quantities.

Temperature of experiment	Time of experiment	Conditions of experiment.	% GB found at end of experiment (Peroxide method)	Remarks
120°C.	2 hours	Stored alone	0.7%	Propene evolved - amount not measured.
140°C.	5½ hrs.	5% Tri-n-butylamine added.	1.5%	-
100°C.	22½ hrs.	Stored alone	6.6%	Propene evolved - amount not measured.
100°C.	64 hrs.	In presence of steel	3.2%	-
100°C.	12 days	" " " "	7.9%	-
100°C.	64 hrs.	5% Tri-n-butylamine added.	0.7%	-
100°C.	12 days	" " " "	1.8%	-

From the value of the rate constant for this reaction, k'_d , at 100°C. given in table III, the amount of GB formed in 22½ hrs., and 64 hrs. would be about 11% and 25% respectively. It is possible that the amount of GB formed in the experiment where the mixture was stored alone for 22½ hrs. at 100°C. was of the order of 11%, since 6.6% was found at the end of the experiment and some had decomposed to give propene. On the other hand, it is clear that the presence of steel or bases retards the reactions, presumably by removal of acid. This means that the reaction is acid catalysed and it would seem that the spontaneous rate, if any, is appreciably slower than that indicated by the rate constants given in table III.

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Attempts were made to determine initial slopes as had been done in the case of the di-ester, two values which were not constant and appeared to increase with increasing acid concentration. This and the fact that no gas evolution occurred in the presence of the other acids indicated that no direct gas evolution occurred from the di-ester and it was suggested that the propene evolved might come from GB formed by some reaction in the system.

Analysis of the liquid residues at the end of the experiments by the Peroxide method showed the presence of GB, the amount depending on the amount of the methylphosphonic acid originally present. Infra-red analysis indicated the presence of traces of GB, but identification of only GB in a mixture containing about 80% of the di-ester and 20% of the acid is extremely difficult.

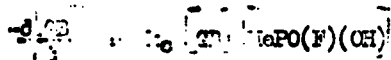
Having obtained the GB content of the mixtures it is possible to work out rate constants for the decomposition of the GB into propene catalysed by the methylphosphonic acid. The results together with the other data are given below.

methylphosphonate -
volatile esters.

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Amount of acid remaining i.e. initial acid less GB mole/l. initial mole ester		Rate constant for decomposition of GB at 100°C hrs. ⁻¹
0.0001	0.0000	0.1980
0.0037	0.0000	0.1537
0.0121	0.0000	0.0894
0.0115	0.0000	0.0696
0.0659	0.0281	0.0397
0.0431	0.0182	0.0249
		2.50 x 10 ⁻²
		2.49 x 10 ⁻²
		2.91 x 10 ⁻²
		3.60 x 10 ⁻²
		4.42 x 10 ⁻²
		5.73 x 10 ⁻²

The rate constants were calculated from the equations:-



the slopes of the curves being measured at the end of the experiments i.e. at the same time as the GB concentrations were determined. The final methylphosphonic acid concentration was used in the calculation, as in reaction with the di-ester it is probably replaced by a weaker acid.

The mean value for the rate constant at 100°C is 3.6×10^{-2} hrs.⁻¹, which agrees well with the value obtained in Table III, viz 3.99×10^{-2} hrs.⁻¹.

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Attempts to obtain rate constants from initial slopes as had been done in the case of the half ester gave values which were not constant and appeared to increase with increasing acid concentration. This and the fact that no gas evolution occurred in the presence of the other acids indicated that no direct gas evolution occurred from the di-ester and it was suggested that the propene evolved might come from GB formed by some reaction in the system.

Analysis of the liquid residues at the end of the experiments by the Peroxide method showed the presence of GB, the amount depending on the amount of the methylphosphonofluoridic acid originally present. Infra-red analysis indicated that presence of traces of GB, but identification of only 4% in a mixture containing about 80% of the di-ester and 20% of the acid is extremely difficult.

Having obtained the GB content of the mixtures it is possible to work out rate constants for the decomposition of the GB into propene catalysed by the methylphosphonofluoridic acid. The results together with the other data are given in Table V.

Table V

Decomposition of Di-isopropyl methylphosphonate -
methylphosphonofluoridic acid Mixtures.

Temperature 100°C.

Amount of acid initially present in moles/initial mole ester	GB found at end of experiment		Amount of acid remaining i.e. initial acid less GB formed moles/initial mole ester	Rate constant for decomposition of GB at 100°C hrs. ⁻¹
	% by weight	in moles/initial mole ester		
0.2601	4.8	0.0621	0.1980	2.50 x 10 ⁻²
0.2137	4.6	0.0600	0.1537	2.49 x 10 ⁻²
0.1421	4.0	0.0527	0.0894	2.91 x 10 ⁻²
0.1115	3.2	0.0419	0.0696	3.60 x 10 ⁻²
0.0659	2.0	0.0262	0.0397	4.42 x 10 ⁻²
0.0431	1.4	0.0182	0.0249	5.73 x 10 ⁻²

The rate constants were obtained from the equation:-

$$-\frac{d[GB]}{dt} = k_c [GB] [MePO(F)(OH)]$$

the slopes of the curves being measured at the end of the experiments i.e. at the same time as the GB concentrations were determined. The final methylphosphonofluoridic acid concentrations were used in the calculation, as in reaction with the di-ester it is probably replaced by a weaker acid.

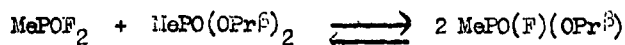
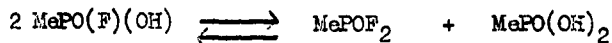
The mean value of the rate constant from Table V is $3.6 \times 10^{-2} \text{ hrs}^{-1}$, which agrees remarkably well with the value obtained in Table III, viz $3.59 \times 10^{-2} \text{ hrs}^{-1}$.

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The nature of the reaction between di-isopropyl methylphosphonate and methylphosphonofluoridic acid is not known. A direct trans-esterification is possible:-



A more likely mechanism, by known reactions, is the disproportionation of the acid into methylphosphonic difluoride and methylphosphonic acid followed by reaction of the di-ester and difluoride to give GB (reverse reaction II).



GB.

7. The effect of fluorides on the decomposition of pure GB.

The mechanism for the disproportionation reaction suggested in P.T.P. 265 involved the separation of the GB into a fluoride ion and a phosphorus containing cation. A possible alternative mechanism suggested by Hudson and Bevan (P.T.P. 330) involves the rupture of the P-O- bond yielding an isopropoxide ion.

It was thought that it might be possible to distinguish between the two mechanisms by investigating the effect of fluoride ion on the reaction, which should be retarded if the first mechanism is correct.

Experiments were carried out with GB to which 2.9% of tributylamine hydrofluoride and 4% excess tributylamine were added and using GB plus 4% tributylamine as controls. Actually the base hydrofluoride was not in fact prepared, but one equivalent of base was added to a solution of a known amount of HF in GB. The results are given in table VI.

Table VI

Effect of fluoride on the thermal decomposition of GB at 120°C.

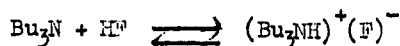
Experiment	Time of storage hours	GB content % by weight		+ Gas evolved moles/initial mole GB			Percentage of original GB decomposed		
		initial	after storage				Total	By Reaction I	By Reaction II
				Total	HF	Propene			
GB + 4% Bu ₃ N + 2.9% Bu ₃ N.F	7 24 47 119	93.1	90.9 86.2 84.6 73.7	Nil Nil 0.006 0.052	Nil Nil 0.001 0.007	Nil Nil 0.005 0.051	2.4 7.4 9.1 20.8	Nil Nil 0.5 5.1	2.4 7.4 8.6 15.7
GB + 4% Bu ₃ N.	7 24 47 119		94.0 90.5 89.1 83.2	Nil Nil 0.003 0.029	Nil Nil Nil Nil	Nil Nil 0.003 0.029	2.1 5.7 7.2 13.3	Nil Nil 0.3 2.9	2.1 5.7 6.9 10.4
GB + solid lithium fluoride.	7 31 119		97.2 [†] 96.1 [†] 79.9 [†]	Nil 0.005 0.084	Nil Not analysed Not analysed	Nil Nil Nil	2.8 3.9 20.1	Nil Not known Not known	2.8 Nil Nil

† The GB did not dissolve any lithium fluoride at room temperature.

+ The figures for HF and propene contain the amounts of these gases combined as isopropyl fluoride and hence the sum of these amounts may exceed the actual observed total.

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It will be seen that the amount of GB decomposed was in fact greater when the hydrofluoride was present than in the controls. This may be due either to catalysis of the decomposition by the tributylammonium ion or to the presence of some free HF, as it is unlikely that, even in the presence of the excess base, the equilibrium



proceeds entirely to the right in this medium. These experiments therefore contribute nothing to the study of the mechanism of reaction II.

As it had been found that lithium chloride was soluble to some extent in GB, it was thought that the fluoride might be slightly soluble and hence provide fluoride ion in the solution. Experiments were carried out in which pure GB was added to tubes containing dried lithium fluoride. The results are also given in table VI. It was found that the decomposition of the GB by both reactions I and II was appreciably retarded as compared with GB stored above. A comparison of the gas evolution from GB alone and in the presence of lithium fluoride is shown in figure 8. This result was quite unexpected and the only explanation which can be advanced is that the catalysis by acid of the decomposition reactions is prevented by removal of the acid by reactions such as:-



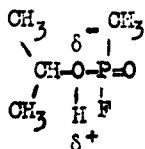
The experiments do not provide any evidence for the mechanism of reaction II, but the marked retardation of the decomposition made the consideration of alkali metal fluorides as stabilisers for technical GB desirable. Experiments carried out to examine this possibility have already been reported (P.T.P. 381).

8. The thermal decomposition of methyl methylphosphonofluoridate.

The difficulty of isolating one of the reactions involved in the decomposition of GB made the consideration of the decomposition of related compounds worthwhile. The obvious choice was methyl methylphosphonofluoridate since this should undergo disproportionation but no olefine-forming reaction. A sample of the compound was prepared but it proved to be unstable at room temperature and a study of its decomposition could not be undertaken.

9. Discussion

Reaction I, the decomposition of GB into methylphosphonofluoridic acid and propene is catalysed by all the acids which may be present as impurities in technical GB. The values of the rate constants and the activation energy for this reaction obtained in the present report do not differ greatly from those previously reported (P.T.P. 265). The mechanism for this reaction previously proposed still holds good, although there is some indication from infra-red spectra that the hydrogen ion is not located at the oxygen of the phosphoryl group and the alternative representation of the transition state involving hydrogen in attack at the oxygen of the isopropoxy group is therefore preferable, i.e.



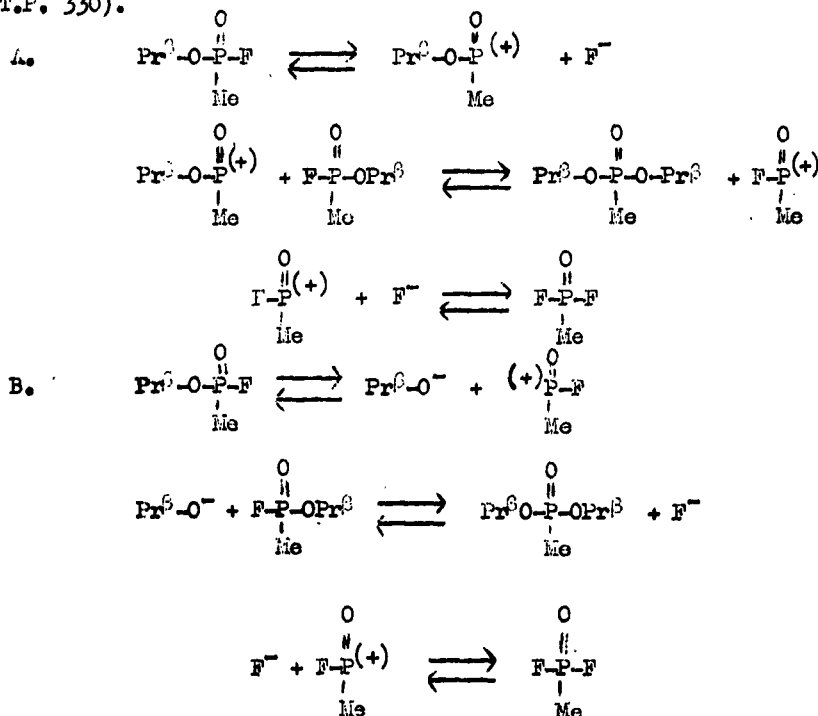
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At the moment no further discussion of the effectiveness of the different acids as catalysts for the reaction is desirable but this may be possible when the results of conductivity measurements now in progress at Porton are available.

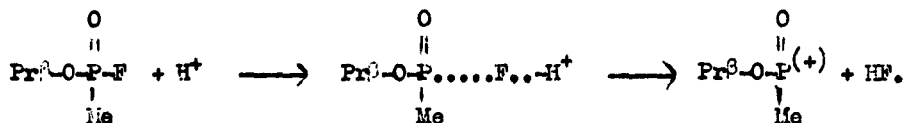
The picture with regard to Reaction II on the other hand is still rather confused. The meaning of the rate constants and activation energies obtained is by no means clear.

It seems certain that in the absence of reaction I this reaction will proceed until an equilibrium is set up. The results reported in Appendix XII to P.T.P. 381 indicate that this probably occurs in GB under practical storage conditions. The amount of GB present at equilibrium will increase with temperature, being about 50% at 25°C. and 80% at 100°C.

As previously noted, two alternative mechanisms for Reaction II have been proposed, the first (A) in P.T.P. 265 and the second (B) by Hudson and Bevan (P.T.P. 330).



Hudson and Bevan (Loc. cit.) suggest that acid catalysis of the forward reaction could be explained according to the first mechanism by assisting the first stage and leading to the formation of undissociated acid:-



In the case of mechanism B, on the other hand isopropanol would be formed.

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It has already been noted that bases retard the forward reaction (P.T.P. 265). The reverse reaction is also retarded by bases and in the presence of steel. This action of bases may be due to competition between two anionoid groups for the phosphorus cation at the second stage, as was suggested in P.T.P. 265. However, the retardation in the presence of steel must be due to removal of acid by reaction with the steel, and the effect of bases is more likely to be due to the same cause.

The present experiments have not made the elucidation of the mechanism of this reaction possible. It is possible that aluminium fluoride would enable a differentiation between the two mechanisms to be made since it readily combines with fluoride ion to yield the fluoaluminate ion, AlF_4^- . If it increased the rate of the disproportionation reaction, mechanism A would be favoured.

The possibility of making GB by the reverse reaction II from methylphosphonic difluoride and di-isopropyl methylphosphonate does not appear to be worthy of consideration. Although the equilibrium mixture at 100°C . should contain 80% of GB, the actual rate of the reverse reaction is rather slow, and it is difficult to prevent the decomposition of GB by reaction I. In the presence of bases or steel when reaction I is retarded, the reverse reaction II is also retarded. A catalyst for reaction II only and a reaction temperature of 120°C . or above might make the process worthwhile. Aluminium fluoride might be suitable if it reacts as suggested above, but the complex fluoride might prove too stable.

Further experiments with aluminium fluoride might be worthwhile, but it has not been possible up to the present to carry out any further work on this problem.

Summary and Conclusions

1. Further work on the thermal decomposition of isopropyl methylphosphonofluoridate (GB) has shown that the reactions involved differ in some respects from the scheme previously suggested.
2. The decomposition consists of the acid catalysed decomposition into propene and methylphosphonofluoridic acid showing second order kinetics, and the simultaneous reversible disproportionation into methylphosphonic difluoride and di-isopropyl methylphosphonate.
3. The decomposition of the di-ester produced in the disproportionation has been shown not to occur in the system so that the reverse disproportionation must be considered.
4. The data previously obtained have been reconsidered in accordance with the later findings and new values for the rate constants obtained. Values of the equilibrium constant for the disproportionation have also been calculated.
5. Other experiments have not enabled the mechanism of the disproportionation reaction to be elucidated and the significance of the rate constants obtained for this reaction is by no means clear.
6. The results obtained for the propene evolution reaction do not differ significantly from those obtained previously and the main conclusions of earlier reports still hold good.

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Acknowledgements

The author is indebted to A.C. Thomas for assistance with the practical work, to J.H. Williams for the analyses of the evolved gases and to L.C. Thomas for the infra-red analyses.

Helpful discussions with Drs. C.W.L. Bevan and R.F. Hudson during their tenure of appointments as vacation consultants at Porton are also acknowledged.

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Appendix I

Calculation of the equilibrium constant for the disproportionation reaction from thermochemical data

Using the values given by Neale (P.T.P. 339), the heat of formation of di-isopropyl methylphosphonate may be calculated as follows:-

(i) Heat of formation from atoms is the sum of:-

$$\begin{array}{rcl}
 \text{CH}_3 \text{ i.e. } 3 \times \text{C-H} & = 3 \times 99.4 & = -298.2 \text{ K.cal./mole} \\
 2 \times \text{iso C}_3\text{H}_7\text{O} & = 2 \times 945.7 & = -1891.4 \text{ K.cal./mole} \\
 \text{P=O} & & = -128 \\
 \text{P-O(Alk.)} & & = -78 \\
 \bar{Z} \\
 2 \times \text{P-O-C(Alk.)} & = 2 \times 95 & = -190 \\
 \hline
 & & = -2585.6
 \end{array}$$

(ii) To obtain the heat of formation from elements in their standard states we add the sum of the heats of atomisation of the elements:-

$$\begin{array}{rcl}
 \text{C}_7\text{H}_{17}\text{O}_3\text{P i.e. } 7 \text{ C} & = 7 \times 171.7 & = 1201.9 \text{ K.cal./mole} \\
 17 \text{ H} & = 17 \times 52.0 & = 884.0 \\
 3 \text{ O} & = 3 \times 59.2 & = 177.6 \\
 \text{P} & = 75.2 & = 75.2 \\
 \hline
 & & 2338.7
 \end{array}$$

(iii) The heat of formation of gaseous di-isopropyl methylphosphonate from elements in their standard states is therefore:-

$$\begin{array}{rcl}
 & & -2585.6 + 2338.7 \text{ K.cal./mole} \\
 & = & -246.9 \text{ K.cal./mole}
 \end{array}$$

The latent heat of vaporisation of the ester, obtained from vapour pressure data (E. Neale; P.T.P. 341) is 14.7 K.cal./mole.

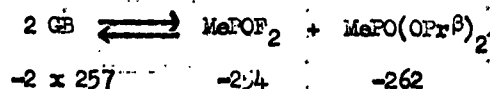
Hence the heat of formation of the liquid ester is:-

$$\begin{array}{rcl}
 & & -246.9 - 14.7 \text{ K.cal./mole} \\
 & = & -261.6 \text{ K.cal./mole}
 \end{array}$$

Neal (P.T.P. 339) gives for the heat of formation from elements in their standard states:-

$$\begin{array}{rcl}
 \text{GB} & -257 \text{ K.cal./mole} \\
 \text{MePOF}_2 & -254 \text{ K.cal./mole}
 \end{array}$$

Taking a rounded off figure of -262 K.cal./mole for the ester, we have for the disproportionation reaction:-



$$\begin{array}{rcl}
 \therefore \Delta F & = -254 - 262 - (-2 \times 257) \\
 & = -2 \text{ K.cal./mole}
 \end{array}$$

... ..

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Now $\Delta F = \Delta H - T\Delta S$

If ΔS is small and can be neglected then:-

$$\Delta F = \Delta H = -2 \text{ K.cal./mole}$$

Using van't Hoff equation, $\ln K_{25} = -\Delta F/RT$

$$\ln K_{25} = \frac{-2000}{1.986 \times 298} = -0.00338$$

$$\log_{10} K_{25} = -0.00147$$

$$\log_{10} K_{25} = 0.00147$$

and $K_{25} = 1.003$

$$\text{Hence at equilibrium } \frac{[\text{MePO}]^2 [\text{MePO(OPr)}]^2}{(\frac{1}{2}[\text{GB}])^2} = 1.003$$

$$\text{and since } [\text{MePO}] = [\text{MePO(OPr)}]$$

$$\text{we can put } [\text{MePO}] = 1.001 \times \frac{1}{2} [\text{GB}] \approx \frac{1}{2} [\text{GB}]$$

$$\text{also } [\text{GB}] + 2[\text{MePO}] = 1$$

$$\therefore \frac{1}{2} [\text{GB}] = [\text{MePO}] = 0.25$$

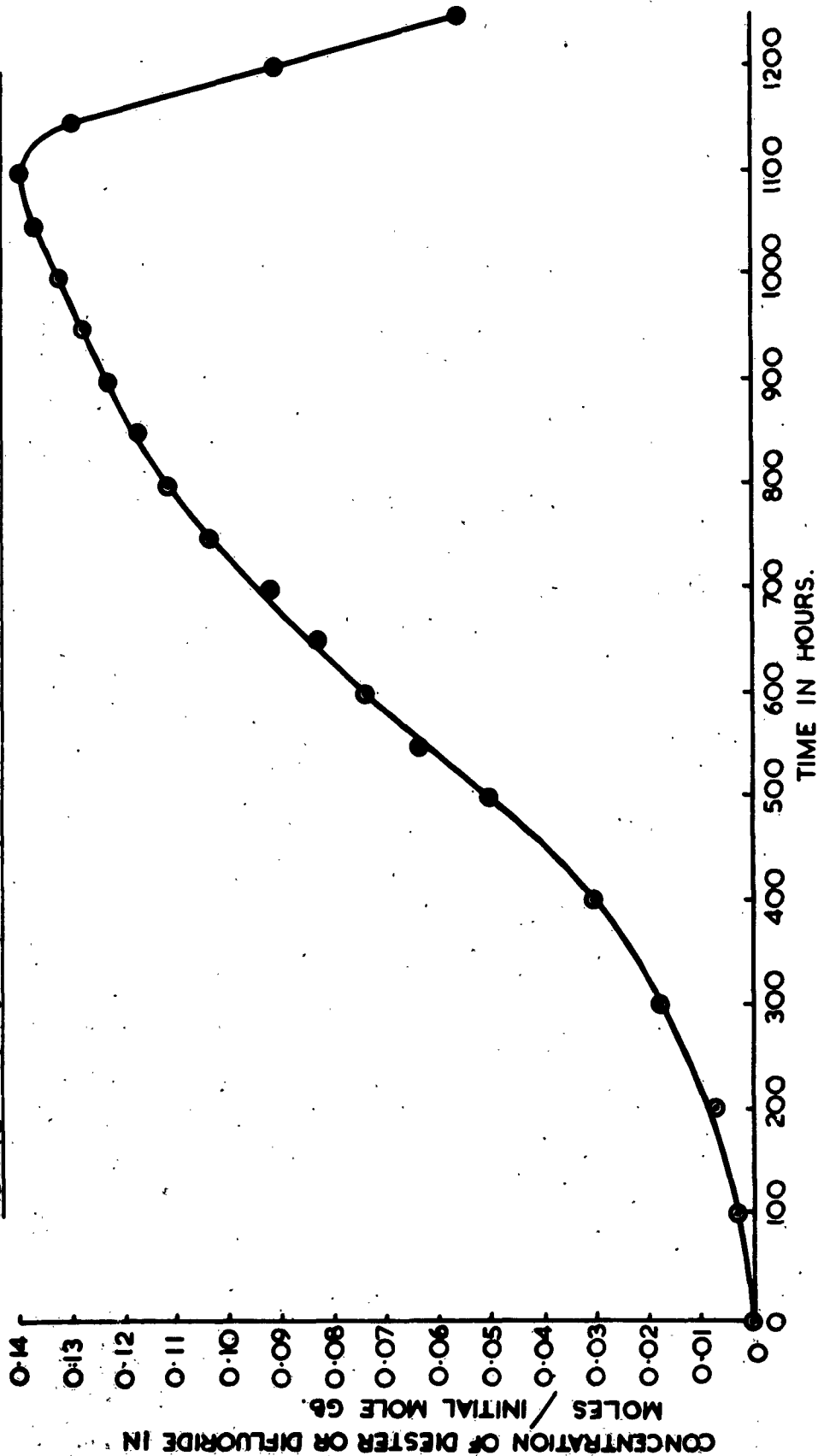
i.e. at 25°C. the equilibrium mixture would contain 50% of GB, 25% of MePO₂ and 25% of di-ester.

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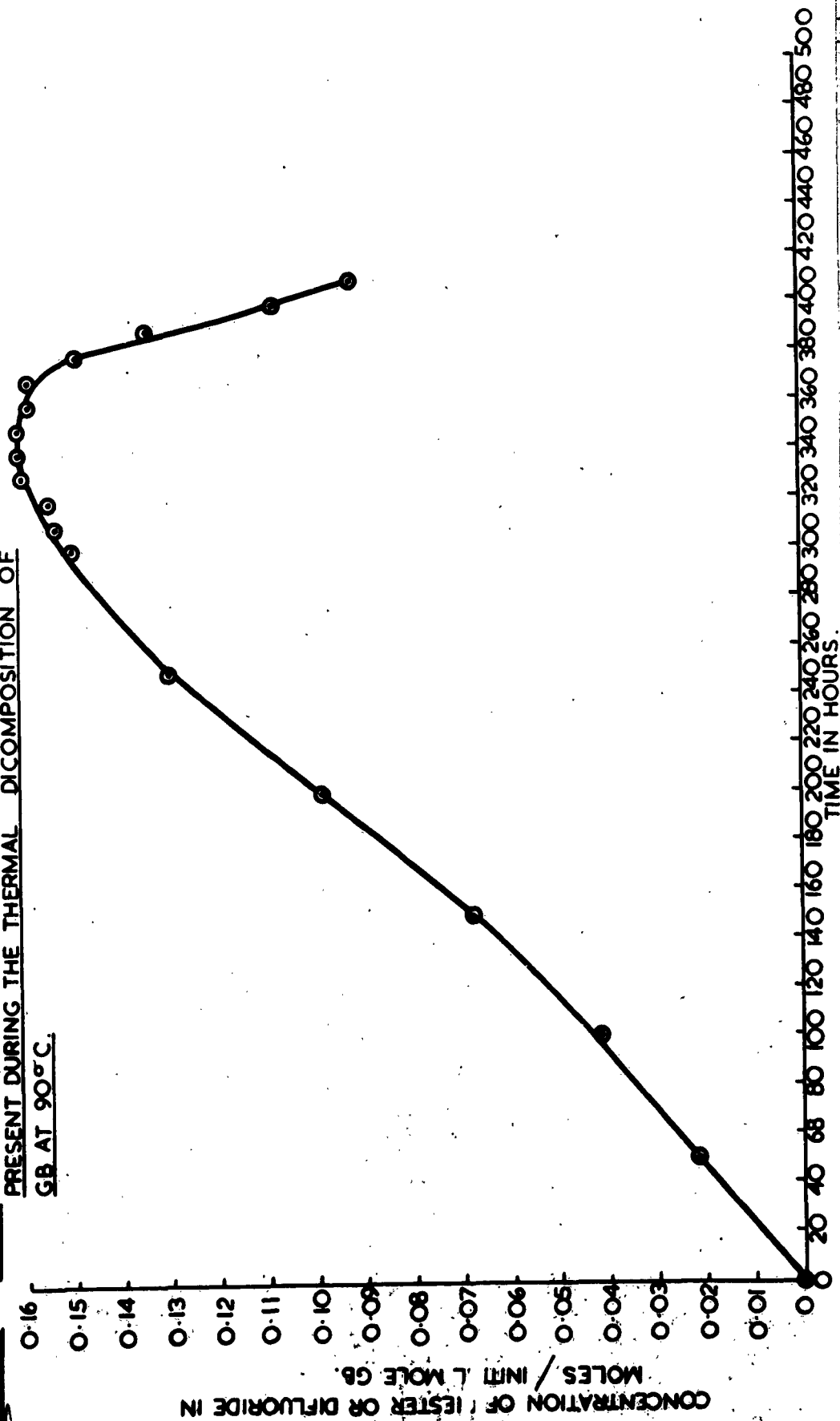
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FIG. 1

VARIATION IN THE AMOUNTS OF METHYL PHOSPHONIC DIFLUORIDE AND DI-ISOPROPYL METHYL PHOSPHONATE PRESENT DURING THE THERMAL DECOMPOSITION OF GB AT 80° C.

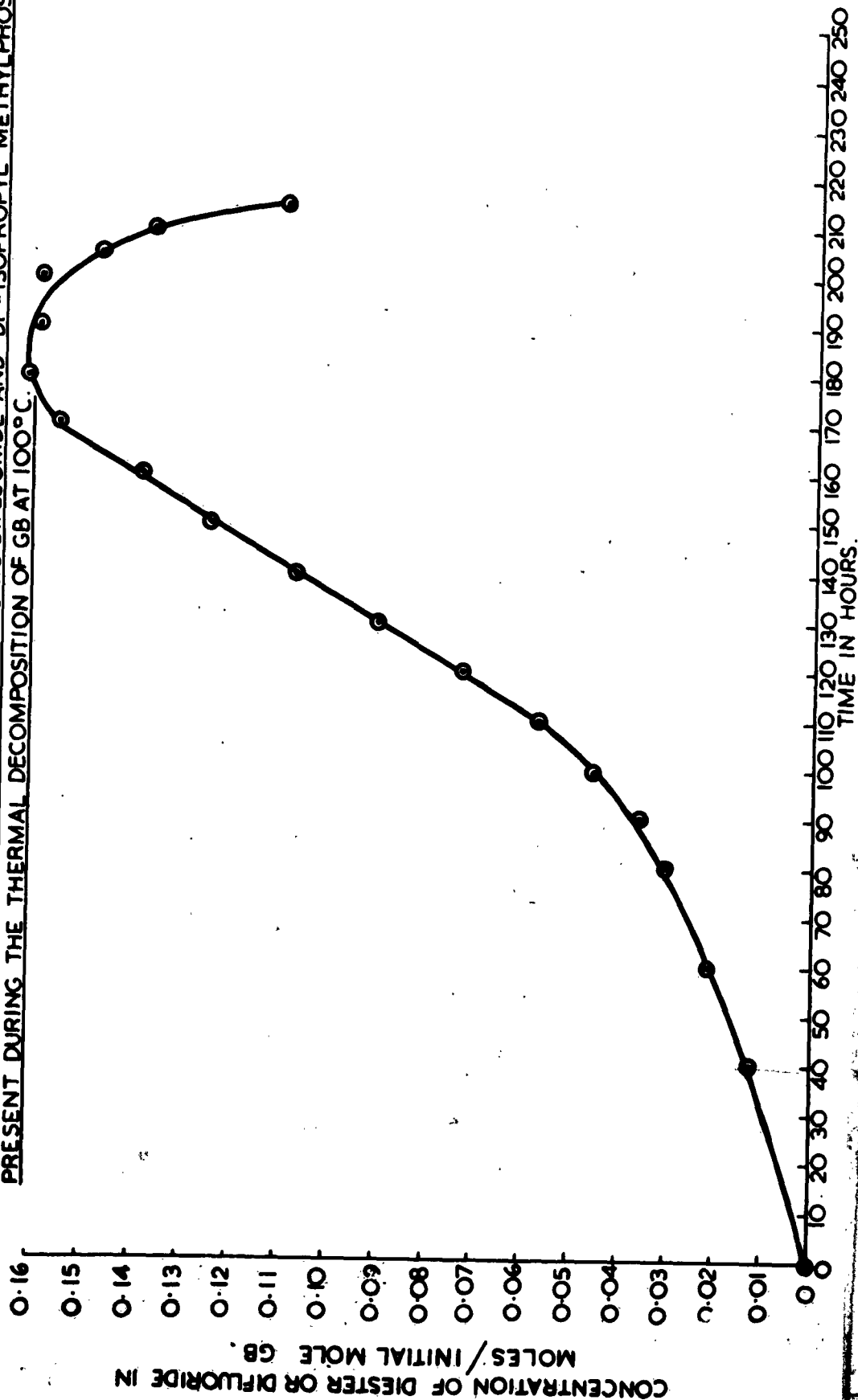


SECRET. **FIG. 2. VARIATION IN THE AMOUNTS OF METHYL PHOSPHONYL DIFLUORIDE AND DI-ISOPROPYL METHYLPHOSPHONATE PRESENT DURING THE THERMAL DICOMPOSITION OF GB AT 90°C.**

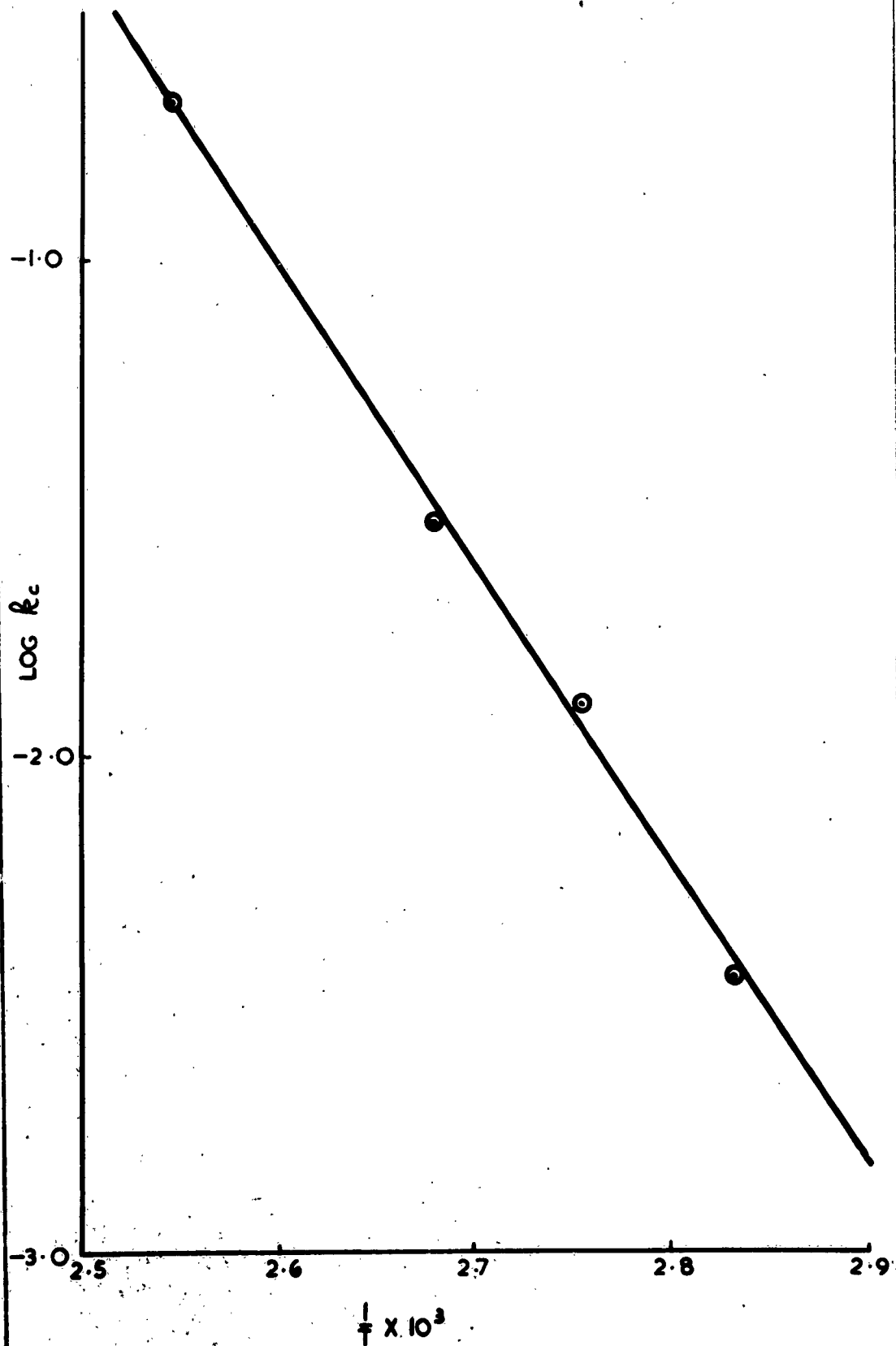


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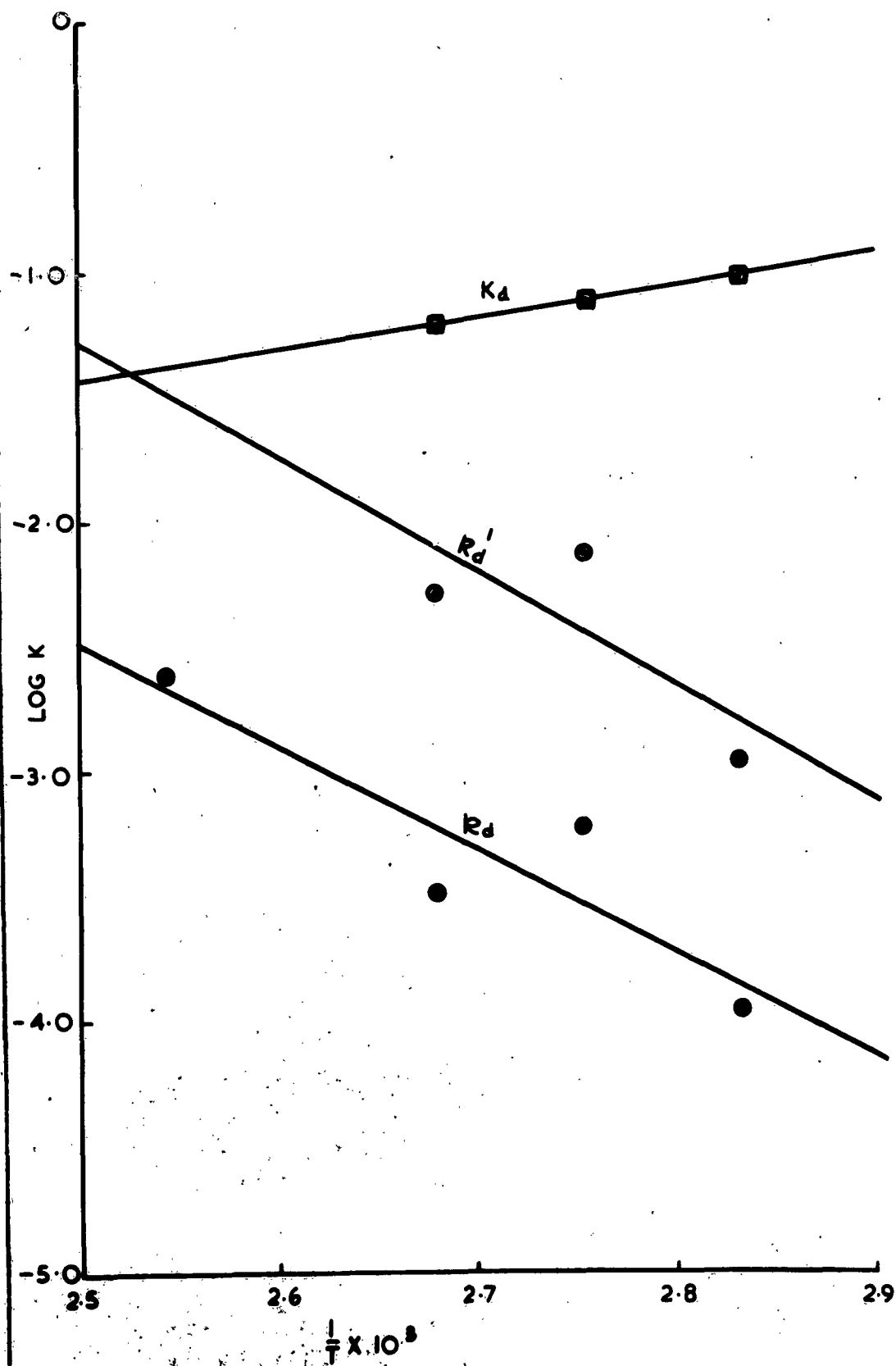
FIG. 3. VARIATION IN THE AMOUNTS OF METHYL PHOSPHONIC DIFLUORIDE AND DI-ISOPROPYL METHYLPHOSPHONATE PRESENT DURING THE THERMAL DECOMPOSITION OF GB AT 100°C.



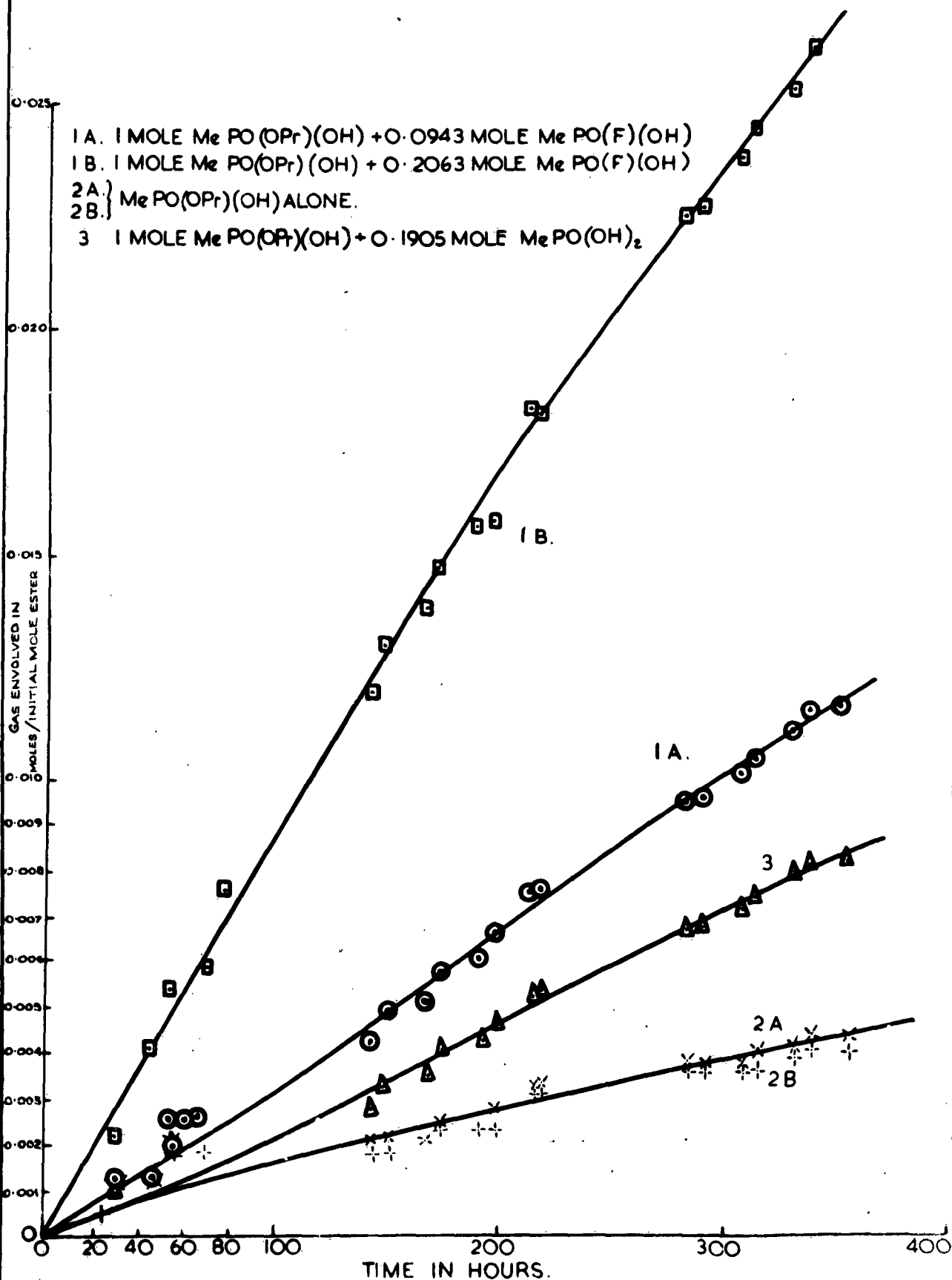
SECRET. FIG. 4. PLOT OF LOG k_c AGAINST THE RECIPROCAL OF THE
ABSOLUTE TEMPERATURE.



SECRET. FIG. 5. PLOTS OF LOG K_d , LOG R_d' AND R_d AGAINST THE
RECIPROCAL OF THE ABSOLUTE TEMPERATURE.



SECRET. FIG. 6. GAS EVOLUTION FROM ISOPROPYL HYDROGEN METHYL -
PHOSPHONATE ACID MIXTURES AT 100°C.



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FIG. 7. GAS EVOLUTION FROM DI-ISOPROPYL METHYL PHOSPHONATE - METHYL PHOSPHONO FLUORIDIC
ACID MIXTURES AT 100°C.

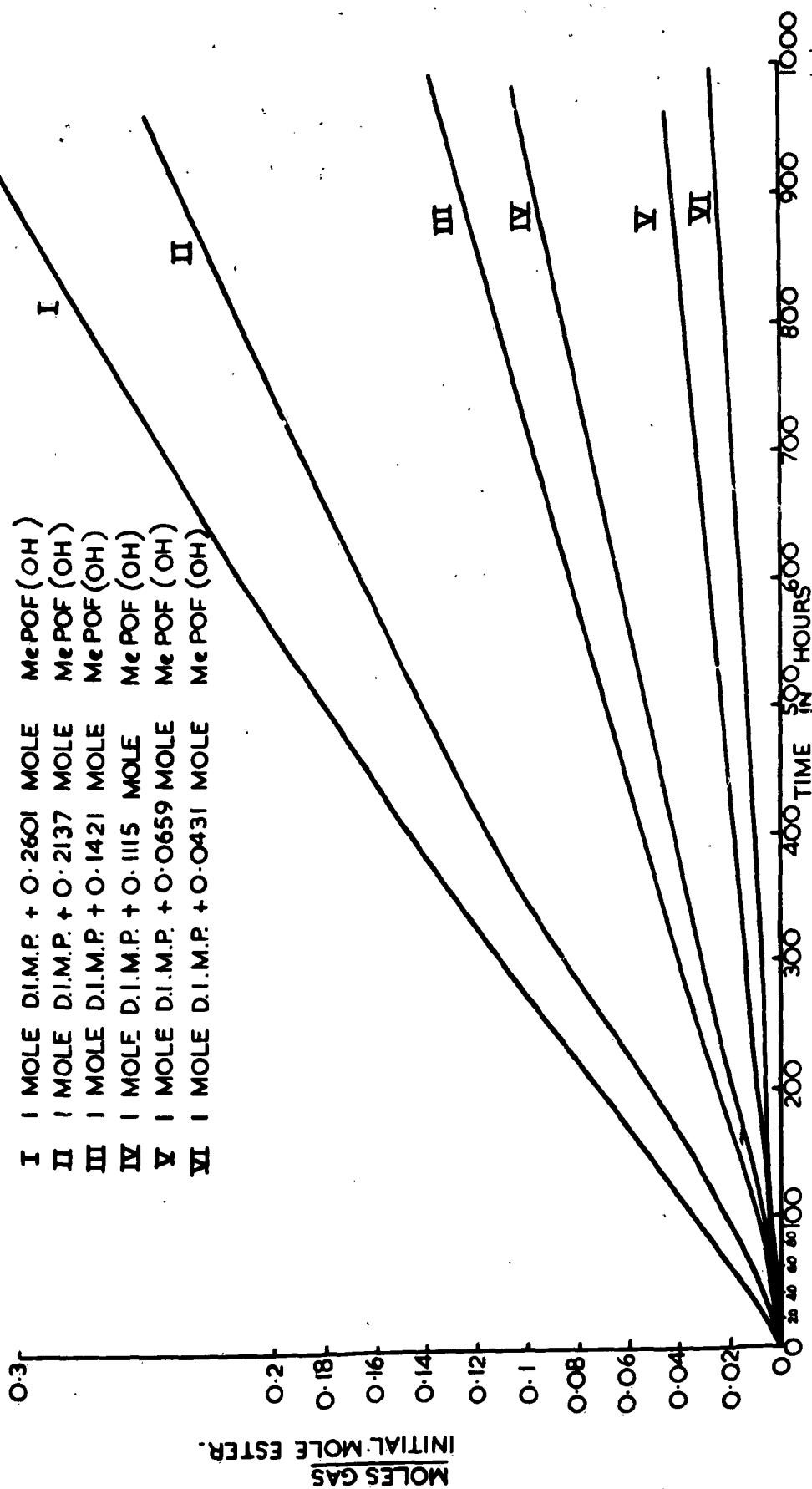
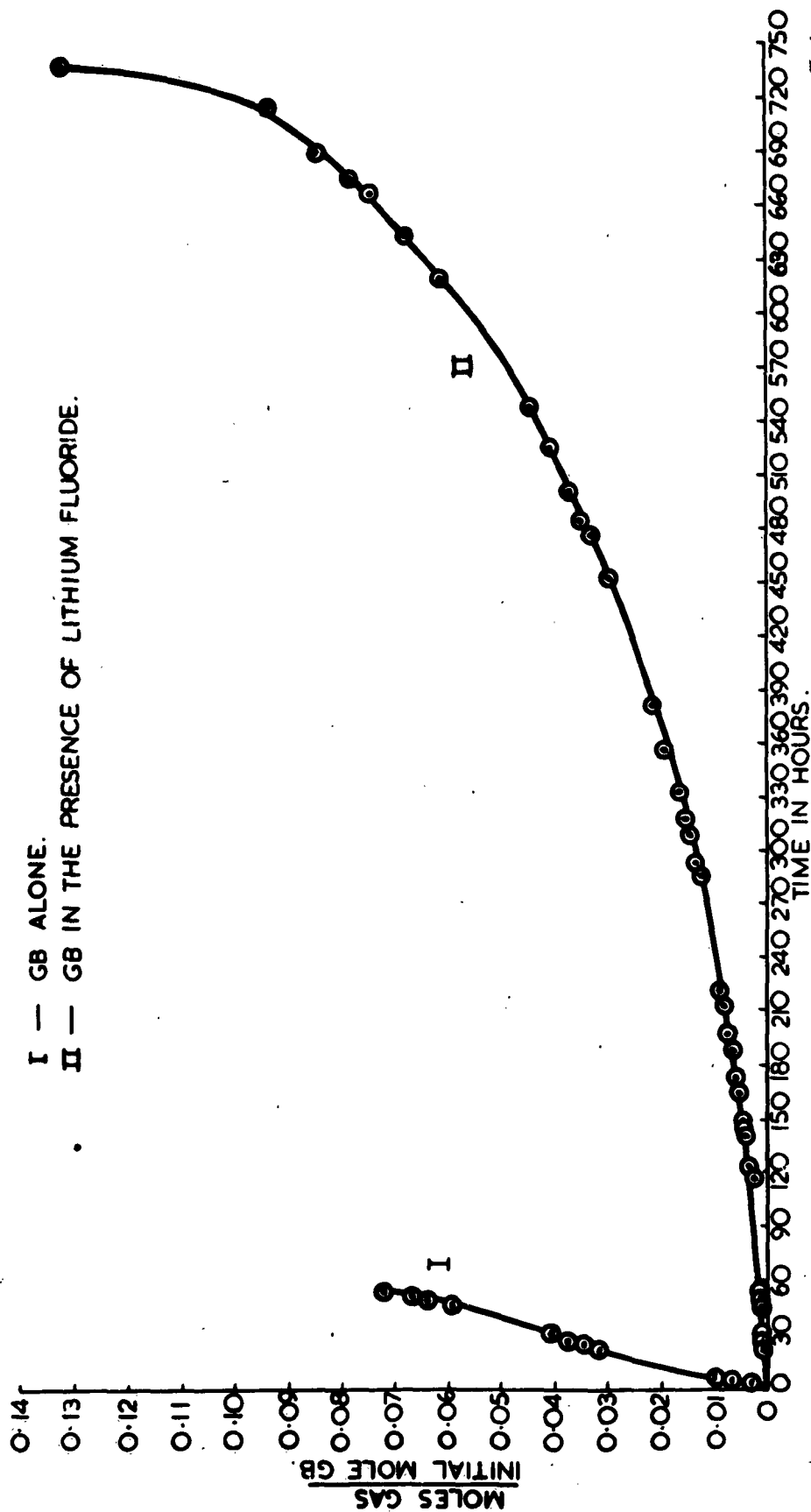


FIG. 8. EFFECT OF LITHIUM FLUORIDE ON THE GAS EVOLUTION FROM GB AT 100° C.



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